

## 2 Thermodynamics of Interfaces

### 2.1 Two-phase Systems

#### 2.1.1 Thermodynamic Approach

As we have discussed, the stability of a disperse system depends on surface conditions of the particles. The surface always appears between two different bulk phases in contact, so that it may also be called an interface but is quite obscure in its structure. (The word, “interface”, may be reserved for the boundary between two condensed phases. However, we ignore the difference between the words, “interface” and “surface”, in the following.) In order to theoretically treat the thermodynamic behavior of the interface in any change of the environments, Gibbs (1931, 1961) introduced a concept of a dividing surface, mathematically constructed between the two phases (see also Chatteraj and Birdi, 1984).

Consider, for instance, a two-phase system of one component, where a liquid is in equilibrium with its vapor (the boundary may be planar or curved). The two bulk phases, ' and ', in reality do not change their states sharply when crossing the interface, but have a region, as shown in Fig. 2.1, over which the density continuously varies (for theoretical thickness, see Lekner and Henderson, 1977 and 1978). However, for convenience, we arbitrarily introduce a sharp dividing surface somewhere around the region.

The extensive (additive) thermodynamic variables, such as the volume, number of moles, internal energy, entropy, etc., of each phase, ' or ', are assumed to con-

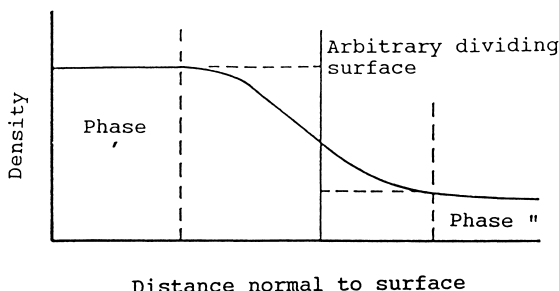


Fig. 2.1 Gibbs' dividing surface.

tinue unchanged up to the hypothetical dividing surface. Thus, if we denote the extended volumes of the two phases by  $V'$  and  $V''$ , respectively, the numbers of moles,  $n'$  and  $n''$ , in  $V'$  and  $V''$  are  $n' = c'V'$  and  $n'' = c''V''$ , respectively, where  $c'$  and  $c''$  are concentrations of the two phases. If the actual total number of moles of the system is  $n$ ,  $n$  will in general differ from the sum of them,  $n' + n''$ , by an excess or deficiency. This excess or deficiency is assigned in the Gibbs model to the interface as a surface quantity and denoted by  $n^s$ . Similarly, we can construct excess quantities (positive or negative) for all extensive variables, which are in turn assigned to the interface and contribute to the surface thermodynamics, as shown below. Obviously, by definition:

$$\text{Total volume: } V = V' + V'' \quad (2.1)$$

Therefore, the dividing surface has a vanishing volume (no thickness). But there is usually a finite number of moles in the surface defined by the excess

$$n^s = n - n' - n'' \quad (2.2)$$

If the total number of moles of the system is assumed not to change, we have

$$dn' + dn'' + dn^s = 0 \quad (2.3)$$

For extensive variables of the system, we can write

$$\text{Internal energy: } U = U^s + U' + U'' \quad (2.4)$$

$$\text{Entropy: } S = S^s + S' + S'' \quad (2.5)$$

Similar relations hold for Helmholtz free energy,  $F$ , Gibbs free energy,  $G$ , etc. The superscript  $s$  denotes surface quantities.

It must be clearly understood that these surface quantities are model-dependent. For instance,  $n^s$  can be negative depending on the choice of a location of the dividing surface. However, although the real system is associated with continuously varying somewhat vague quantities across the surface, the present convention is to allow us to handle the surface quantities by clear definitions of Gibbs' excess quantities. Guggenheim (1940), on the other hand, introduced a little more realistic definition of the surface phase with some volume (see also Jaycock and Parfitt, 1981). But we use the Gibbs formalism.

We can easily make our thermodynamic treatment of the system to include many components by adding matter to the phases (chemical work, which could also be related with chemical reactions or moving between phases). The first and second law of thermodynamics then summarize that the internal energy of the ' phase changes for an arbitrary set of infinitesimal variations from equilibrium, as follows.

$$dU' = TdS' - p'dV' + \sum_i \mu'_i dn'_i \quad (2.6)$$

where  $T$  is the absolute temperature of the system and  $\mu'_i$  is the chemical potential of the  $i$ -th component in the ' phase, defined by

$$\mu'_i = \left( \frac{\partial U'}{\partial n'_i} \right)_{S', V', n'_j}, \quad (i \neq j) \quad (2.7)$$

The chemical potential is usually defined through Gibbs' free energy, which is, for the ' phase,  $G' = U' + p'V' - TS' = \sum_i \mu'_i n'_i$ . Note that the chemical potential is a function of  $T$ ,  $p$ , and the numbers of moles. Similarly for the '' bulk phase

$$dU'' = TdS'' - p''dV'' + \sum_i \mu''_i dn''_i \quad (2.8)$$

For the surface, which has an area  $A$ , with a surface tension  $\gamma$ , but no volume

$$dU^s = TdS^s + \gamma dA + \sum_i \mu^s_i dn^s_i \quad (2.9)$$

We know the chemical potentials,  $\mu'_i$  and  $\mu''_i$ , of different phases in thermal equilibrium are numerically the same. We show in the following that  $\mu^s_i$ , which is arbitrarily defined, is also equal to them. Note that the chemical potential is an intensive variable.

When a thermodynamic reversible process occurs under a constant total volume at fixed temperature, it must satisfy the minimum condition of the Helmholtz free energy,  $F$ , of the total system in equilibrium ( $dF=0$  at the equilibrium). Since  $dV = dV' + dV'' = 0$ ,  $dT=0$ , and  $dU = dU' + dU'' + dU^s$ , we have

$$\begin{aligned} dF &= d(U - TS) = dU - TdS \\ &= (p' - p'')dV'' + \gamma dA + \sum_i (\mu'_i dn'_i + \mu''_i dn''_i + \mu^s_i dn^s_i) \end{aligned} \quad (2.10)$$

If the vapor phase, '', is a spherical bubble (no gravity),  $p'' - p' = 2\gamma/R$ , where  $R$  is the radius, and  $dV'' = \frac{1}{2}RdA$ . Thus, we find

$$(p' - p'')dV'' + \gamma dA = 0 \quad (2.11)$$

This relation holds in general since the system does not make any mechanical work at constant volume (Exercise 2.6). Using Eq. 2.2, we find

$$dF = \sum_i (\mu'_i - \mu^s_i) dn'_i + \sum_i (\mu''_i - \mu^s_i) dn''_i \quad (2.12)$$

Since  $dF=0$  for the isothermal process at constant volume, and  $dn'_i$  and  $dn''_i$  are arbitrary

$$\mu'_i = \mu''_i = \mu^s_i \equiv \mu_i \quad \text{for all } i \quad (2.13)$$

Namely, the chemical potential does not depend on phases in equilibrium. This holds irrespective of the location of the dividing surface and, we know, is a very reasonable result.

Equation 2.13 simplifies the expression of  $dU$  and  $dF$ . From Eqs. 2.6, 2.8, and 2.9 we have

$$dU = TdS - p'dV' - p''dV'' + \gamma dA + \sum_i \mu_i dn_i \quad (2.14)$$

Suppose that we choose  $S$ ,  $V'$ ,  $V''$ ,  $A$ , and  $n_i$  (all  $i$ ) such that, with a small  $\varepsilon$ ,  $dS = \varepsilon S$ ,  $dV' = \varepsilon V'$ ,  $dV'' = \varepsilon V''$ ,  $dA = \varepsilon A$ , and  $dn_i = \varepsilon n_i$ . We write that  $dU = \varepsilon U$  with the same value of  $\varepsilon$ . We substitute these into Eq. 2.14. The new relation holds for any value of  $\varepsilon$  as long as  $T$ ,  $p'$ ,  $p''$ ,  $\gamma$ , and the composition (so  $\mu_i$ ) are kept unchanged. (This procedure is the same as we make the size of the system uniformly larger or smaller. Mathematically,  $U$  is a homogeneous function of those variables.) Let  $\varepsilon = 1$ , then we have

$$U = TS - p'V' - p''V'' + \gamma A + \sum_i \mu_i n_i \quad (2.15)$$

This relation, Eq. 2.15, is called the fundamental equation (or Euler's equation) of thermodynamics because it contains all possible thermodynamic information about a system (Leichl, 1980; Exercise 2.7). If we take a differential of Eq. 2.15 on both sides and note Eq. 2.14, we find

$$SdT - V'dp' - V''dp'' + Ad\gamma + \sum_i n_i d\mu_i = 0 \quad (2.16)$$

This is the Gibbs-Duhem equation for the two-phase system. In particular, for the surface,

$$S^s dT + Ad\gamma + \sum_i n_i^s d\mu_i = 0 \quad (2.17)$$

This is the Gibbs adsorption equation which may be used for determining the surface excess quantities.

Equation 2.17 tells how the surface tension varies with temperature and  $\mu_i$ . However, the pressure dependence  $(\partial\gamma/\partial p)_{T,A}$ , for the planar surface which cannot be defined in the Gibbs model, has been understood as due to the change in molar volume when a molecule goes from the bulk to the surface (see Eq. 2.35 below). The dependence seems to be small for a liquid according to Kahlweit (1970) and Jho et al. (1978). The value for the oil/water interface is about  $10^{-9}$  cm<sup>3</sup>/cm<sup>2</sup> (Motomura et al., 1983). For the temperature dependence, the surface tension is known to decrease until it vanishes at the critical temperature,  $T_c$ . More specifically, for a closed (i.e. constant composition) one-component system with a planar interface, we empirically have (Guggenheim, 1945)

$$\gamma = \gamma_o [1 - (T/T_c)]^\alpha, \quad \alpha = 1.2 \quad (\gamma_o : \text{a constant}) \quad (2.18)$$

(According to Grosse (1962),  $\alpha$  is closer to unity for metals.) Thus,  $\partial\gamma/\partial T < 0$ . This implies that thermal expansion loosens the average molecular attraction. Then, from Eq. 2.17 for a one-component system, we obtain the heat absorbed during the surface expansion by  $dA$  at constant temperature (Exercise 2.8).

$$Q = -T \left( \frac{\partial\gamma}{\partial T} \right)_{p, [\mu_i]} dA \quad (2.19)$$

By combining this with the surface version of Eq. 2.15 for the closed system, the internal energy per unit area is found as follows.

$$\frac{U^s}{A} = \gamma - T \left( \frac{\partial\gamma}{\partial T} \right)_{p, [\mu_i]} \quad (2.20)$$

Note that  $U^s/A$  is different from the surface tension, which is the surface Gibbs free energy per unit area (Exercise 2.9). The importance is that  $U^s/A$  is nearly constant against temperature.

The surface tension depends on the surface curvature. This is particularly important for very small drops or bubbles, which appear in nucleation (see, in particular, Sec. 3.4). According to Melrose (1968),

$$\gamma = \gamma^o \left( 1 - \frac{\delta}{R_m} \right) \quad (2.21)$$

where  $\delta$  is the measure of the surface thickness ( $\sim \text{\AA}$ ) and  $R_m$  may be positive or negative, but can only be found by observation. Fisher and Israelachvili (1980) observed that for several organic liquids the surface tension remained unchanged down to radii of curvature as low as 0.5 nm. Christenson (1985) found the surface tension for water unchanged down to radii of 2 nm.

Now we can formally define the surface tension. If it does not depend on the curvature, from Eqs. 2.9 and 2.10 we can write

$$\gamma = \left( \frac{\partial U^s}{\partial A} \right)_{S^s, [n_i^s]} = \left( \frac{\partial F}{\partial A} \right)_{T, V', V'', [n_i]} \quad (2.22)$$

There are many ways to measure the surface tension for liquid-vapor interfaces (Adamson, 1990). The value is closely related to surface quantities.

The Gibbs adsorption equation, Eq. 2.17, gives

$$Ad\gamma + \sum_i n_i^s d\mu_i = 0 \quad (2.23)$$

at constant temperature and pressure. By defining a surface concentration of the  $i$ -th component by

$$\Gamma_i = \frac{n_i^s}{A} \quad (2.24)$$

we have the Gibbs adsorption isotherm

$$d\gamma = -\sum_i \Gamma_i d\mu_i, \quad (T, p: \text{constant}) \quad (2.25)$$

The quantity  $\Gamma_i$  designates the adsorption. We must note from Eq. 2.24 that  $\Gamma_i$  depends on the location of the Gibbs dividing surface through  $n_i^s$  and the area,  $A$ , if curved. The location can be defined in various ways. Usually, one of  $\Gamma_i$ 's is equated to null to fix the location. As will be briefly shown later, a new approach in defining the location has been proposed by introducing a surface volume like Guggenheim (1940).

As an example for Gibbs' method, consider a choice,  $\Gamma_1=0$ , to fix the location of the dividing surface at least in the mathematical treatment. Then, the surface excess quantities are accordingly determined referring to the choice. We denote the quantities by  $\Gamma_i^1$  ( $\Gamma_i^1 = 0$ ). For a two-component system, we can write

$$d\gamma = -\Gamma_2^1 d\mu_2 \quad (2.26)$$

We note that  $\mu_2$  can be written in terms of the activity,  $a_2$ , of component 2 as  $\mu_2 = \mu_2^0 + k_B T \ln a_2$  in the bulk solution, where  $\mu_2^0$  is the standard state chemical potential and  $k_B$  is the Boltzmann constant. If the system is an ideal and dilute solution of component 2 (nonionizing), the activity is proportional to the molar concentration,  $c_2$ , and we can rewrite Eq. 2.26 as follows.

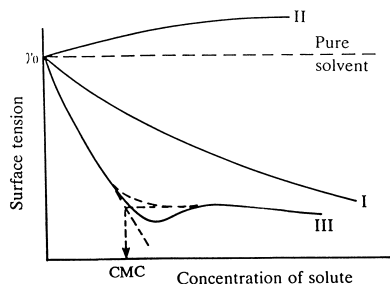
$$\Gamma_2^1 = -\frac{1}{k_B T} \frac{d\gamma}{d \ln c_2} = -\frac{c_2}{k_B T} \frac{d\gamma}{dc_2} \quad (2.27)$$

(Note that the chemical potential is equal to that of any phase.)

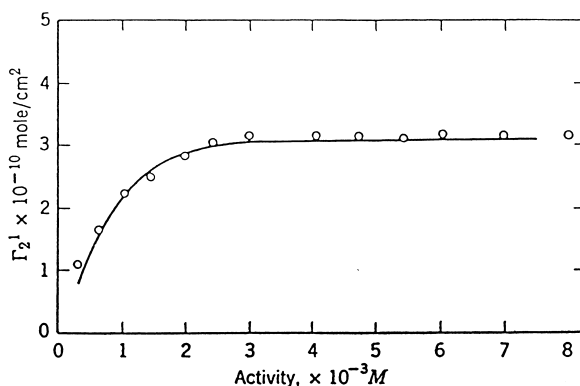
Equation 2.27 gives the relationship between the relative adsorption and the solution concentration  $c_2$ , as long as the  $c_2$ -dependence of the surface tension is concerned. If  $d\gamma/dc_2 < 0$  (i.e. the component lowers the surface tension),  $\Gamma_2^1$  is also positive and there is actually a surface excess of solute. The solute is then said to be surface active. If it is highly surface active (i.e. an amphiphilic substance, such as a detergent), the surface tension decreases very fast but ceases to do so at around the concentration of  $10^{-3}$  or  $10^{-2}$  M with the formation of micelles (see Sec. 9.2). Otherwise, if the concentration increases, the more surface deficiency occurs (i.e. the solute is repelled away from the interface) like lyophilic solute or ionic salts, (Fig. 2.2).

The most convincing experimental proof of the Gibbs equation is the work of Tajima et al. (1970) by means of a tracer method (Fig. 2.3). The figure shows saturation, since there must be a limitation on the number of molecules of a finite size at the surface. Historically, the experimental check of Eq. 2.27 was made by obtaining the value of  $\ln c_2$  after analyzing the liquid scooped-up from the aque-

**Fig. 2.2** Behavior of  $d\gamma/dc_2$  against the concentration of solute  $c_2$  (Davies and Rideal, 1963, with permission from Academic Press).



**Fig. 2.3** Verification of the Gibbs equation (Tajima, et al., 1970, with permission from the Chem. Soc. Japan).



ous surfactant solution (McBain and Humphreys, 1932, and see Defay et al., 1966). Recently, however, radioactive tracers have been used to determine surface excess quantities at the liquid-vapor interface. The solute to be studied is labeled with a radioactive isotope which emits weak  $\beta$  radiation, such as  $^3H$  or  $^{14}C$ . Since the range of such  $\beta$  penetration is small in condensed media (about 30 mg/cm<sup>2</sup> or less), the  $\beta$  detected above the interface will be those coming from the thin surface layer of about 0.05 mm thick (Hiemenz, 1977).

In this measurement, we must note that Gibbs equation may have to be modified for ionizing substances. For instance, the absorption of sodium dodecyl sulfate, NaA, at the interface with water. It dissociates completely at the surface and the activity is given by the product of the ionic activities of  $Na^+$  and  $A^-$ , if the surface as a whole is electrically neutral. Then, if dilute,  $c_2$ , i.e.  $c_{NaA}$ , in Eq. 2.27 must be replaced by its square (Tajima et al., 1970). If, in addition, a large excess of a simple sodium salt (say NaCl) is added, then the system will be held at constant ionic strength. As stated before about ionic salts, chloride ions are negligibly adsorbed in air-water interface and the chemical potential of both  $Na^+$  and  $Cl^-$  will be held essentially constant irrespective of the concentration of NaA. In Eq. 2.27,  $c_2$  is given by that of  $A^-$ . As another example, an electrolyte can change to an electrical neutral substance by hydrolysis ( $X^- + H_2O = HX + OH^-$ ) and the neutral substance is surface active (Salley et al., 1950; Sekine et al. 1970). For precautions in the tracer technique, see Agrawal and Neuman (1988).

In contrast to the Gibbs method of determining the location of the dividing surface, Hansen (1962) introduced a new approach, as stated before (also see Motomura and Aratono, 1987). A surface phase, which has a volume, may be introduced just like in the approach of Guggenheim (1940), so that Eq. 2.17 is rewritten for a planar surface ( $p' = p'' \equiv p$ ) as, referring to per unit area,

$$d\gamma = -s^s dT + v^s dp - \Gamma_\alpha d\mu' - \Gamma_\beta d\mu'' - \Sigma \Gamma_i d\mu_i \quad (2.28)$$

Here,  $\Gamma_\alpha$  and  $\Gamma_\beta$  denote respectively the concentrations in the surface phase of the components,  $\alpha$  and  $\beta$ , which are dominant in the ' and '' phases. These two surface concentrations are treated separately from other components. In the Gibbs method, there is no surface volume, so that  $v^s = 0$  in Eq. 2.28, and the specific choice of  $\Gamma_i$  is such that  $\Gamma_1 = 0$ . These two arbitrary choices are replaced by

$$\Gamma_\alpha = 0, \quad \Gamma_\beta = 0 \quad (2.29)$$

in the new approach. But how other concentrations are accordingly modified is not easily understood. At any rate, we may denote them by  $\Gamma_i^H$  and write Eq. 2.28, as follows.

$$d\gamma = -s^H dT + v^H dp - \Sigma \Gamma_i^H d\mu_i \quad (2.30)$$

Now, we can write

$$d\mu_i = d\mu'_i = -s'_i dT + v'_i dp + \Sigma_j (\partial\mu_i / \partial n'_j) dn'_j \quad (2.31)$$

Substituting this into Eq. 2.30, we have

$$d\gamma = -\Delta s dT + \Delta v dp + \Sigma_i \Sigma_j \Gamma_i^H (\partial\mu_i / \partial n'_j) dn'_j \quad (2.32)$$

where

$$\Delta s = s^H - \Sigma_i \Gamma_i^H s'_i, \quad \Delta v = v^H - \Sigma_i \Gamma_i^H v'_i \quad (2.33)$$

At constant temperature and pressure, Eq. 2.30 gives

$$d\gamma = -\Sigma_i \Gamma_i^H d\mu_i, \quad (T, p: \text{constant}) \quad (2.34)$$

This is exactly the same form as Eq. 2.25, but we must note the difference in the definition of the surface concentrations. Equation 2.32, however, allows us to estimate the pressure dependence of the surface tension, which is discussed previously, i.e.



$$\left(\frac{\partial \gamma}{\partial p}\right)_{T, n_i'} = \Delta v \quad (2.35)$$

Here, we can note that  $\Delta v$  is the volume change per unit surface area when molecules move from the ' phase to the surface. The new approach has been applied to investigating of the behavior of micelles and ionic surfactants (Motomura et al., 1990).

### 2.1.2 Computer Simulation of Interfaces

Recently, computers have been indispensable tools in modeling the physical structures of interfaces in terms of statistical mechanics. Two most popular types of simulation procedure have been utilized: the Monte Carlo (MC) and molecular dynamics (MD) methods. The former is probably easier to apply but is limited to static properties. The MD method is capable of providing additional information on time-dependent properties (see Nicholson and Parrsonage, 1982; Rowlinson and Widom, 1982; Allen and Tildesley, 1987).

In either method,  $N$  molecules (or ions) are assumed to be in a small box of volume  $V$  at temperature  $T$ . Those molecules are under some mutual interaction, like Lennard-Jones (12,6) type. Their initial distribution function near, say, a liquid-vapor interface may be suggested by experimental results on the surface tension, surface energy and adsorption, such as  $\Gamma_i^1$ , etc. In computer simulation, their positions are varied in succession according to the probability of random numbers (MC) or the classical equation of motion (MD). Thus, we can successively compute the total interaction energy,  $E((x,y,z)^N)$  as a function of positions of  $N$  molecules (or ions) and corresponding thermodynamical functions.

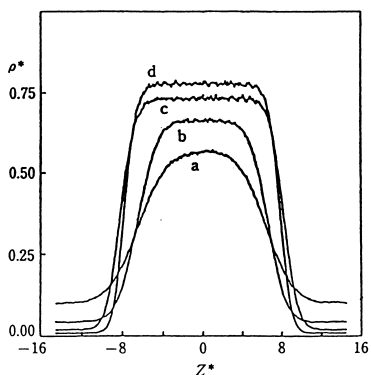
The number  $N$  cannot be made too large (in practice,  $N$  is about 5000) even with a very large computer. In order to eliminate any effect of the boundary of the cell the periodic boundary conditions are usually used to make the system infinitely large. This modification may introduce a spurious correlation effect related to the periodic assumption. This effect can be reduced by a minimum image convention. This convention restricts the calculation of the interaction energy of molecule  $i$  either with  $j$  or with one of its periodic images,  $j'$ ,  $j''$ , etc., whichever is closest to  $i$ . When the system contains a planar surface, the periodic boundary conditions are applied only in the direction parallel to the surface. Other boundaries (parallel to the planar surface) of the basic cell are assumed to reflect approaching molecules.

In the MC method, the random procedure is operated as follows. One molecule is chosen at random in the box and then given a displacement, also randomly chosen. This procedure is repeated and a sequence of states is generated such that each state occurs with a probability proportional to its Boltzmann factor,  $\exp(-E((x,y,z)^N)/RT)$ . Thus, the sequence is specified by fixed values of  $N$ ,  $V$ , and  $T$ , for which the most probable configurations, or distribution functions, can be found. The practical techniques are described by Hansen and McDonald (1976).

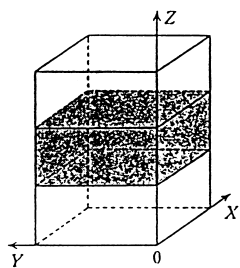
In the MD technique, the computer first calculates the force on each molecule arising from all the other molecules and then, by solving Newton's equation of motion, determine the evolution of an assembly of  $N$  molecules (limited to classical cases). Here, the initial condition may be so chosen as that all the particles are initially at rest. This computation is done simultaneously and continuously for all the molecules in the box. This process may be repeated many times until there is no change in the internal energy and other computed properties of the system. At this point, the system is considered to be in thermal equilibrium corresponding to fixed values of  $N$ ,  $V$ , and the internal energy. The temperature, of course, must be checked by the average kinetic energy of the molecules.

A properly executed computer simulation, whether MC or MD, is regarded as providing the exact solution to any well-defined system. The correctness of the results depends on the type of the interaction potentials. Conversely, the comparison of the results with experiments can verify the potentials used, though they may not be unique. In conclusion, computer simulations provide the most useful theoretical tools available for studying various important phenomena, as shown below for modeling surfaces.

Figure 2.4 shows the density profiles calculated by Nijmeijer et al. (1988) by means of the MD technique. They assumed that the molecules interact one another obeying the Lennard-Jones type,  $V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ , where  $\epsilon$  and  $\sigma$  are the Lennard-Jones potential energy and distance parameter, respectively. The basic



**Fig. 2.4** Density Profile at the vapor-liquid-vapor interface.  $T^* = k_B T / \epsilon = 1.00$  (a), 0.90 (b), 0.80 (c), and 0.72 (d).  $\rho^* = \rho \sigma^3$ .  $Z^* = z / \sigma$  (see Eq. 2.36 for  $z$ ; Nijmeijer et al., 1988, with permission from AIP).



**Fig. 2.5** Basic cell (liquid in the middle).

cell used for the simulation contains  $10^4$  molecules is depicted in Fig. 2.5. The liquid phase is located at the middle height of the cell, so that there are two liquid-vapor interfaces.

Figure 2.4 shows that, as the temperature rises,  $\rho_l$  decreases,  $\rho_v$  increases, and the surface becomes thicker. The experimental density profile can locate the Gibbs dividing surface (see Exercise 2.11). The density profile is often approximated by (Chapera et al., 1977; Lekner and Henderson, 1978)

$$\rho(z) = \frac{1}{2}(\rho_l + \rho_v) + \frac{1}{2}(\rho_l - \rho_v) \tanh \left[ \frac{2(z - z_0)}{D} \right] \quad (2.36)$$

where  $z_0$  is the location of the Gibbs dividing surface. The parameter,  $D$ , stands for the surface thickness, which is given by

$$D = -(\rho_l - \rho_v) \left( \frac{d\rho(z)}{dz} \right)^{-1}_{z=z_0} \quad (2.37)$$

It is interesting to note that the value of  $D$  increases with the width of the cell due to capillary fluctuations. These are suppressed if their wavelengths are longer than the width of the cell (Rowlinson and Widson, 1982, §4.9).

The most important thermodynamic property of the interface is the surface tension. In the simulation, the surface tension is defined in terms of the normal and the tangential component,  $p_n$  and  $p_t$  respectively, of the pressure tensor.

$$\gamma = \int_{-\infty}^{\infty} [p_n(z) - p_t(z)] dz \quad (2.38)$$

In equilibrium, we expect from mechanical stability that the normal component is equal to the pressure of the bulk phases. The treatment of the pressure tensor could be provided by the theory of elasticity and various acceptable expressions for the pressure tensor have been proposed (see reviews of Navascués, 1979, and Schofield and Henderson, 1982). An expression easily applicable for simulation is given by

$$\gamma A = \left\langle \sum_{i < j} \left( r_{ij} - \frac{3z_{ij}^2}{r_{ij}} \right) \frac{du(r_{ij})}{dr_{ij}} \right\rangle \quad (2.39)$$

where  $u(r_{ij})$  is the interaction energy between molecule  $i$  and  $j$ , with distance  $r_{ij}$ . The summation covers all pairs of molecules near the interface of area  $A$ . The angle brackets denote an average over an MD (micro-canonical) or MC (canonical) simulation. It is claimed that the accuracy is around  $\pm 10\%$  for an MC simulation of 250 molecules (Rowlinson and Widom, 1982, p. 182).

The computer simulation is a powerful tool to investigate detailed structures, including molecular orientations, of liquid-vapor interfaces of water (Matsumoto and Kataoka, 1988, giving also the surface potential of 0.162 V; Townsend and Rice, 1991). The values of the surface tension of water obtained by Matsumoto and Kataoka at various temperatures were a little less than half of the experimental values.

## 2.2 Monolayers and Bilayers

Molecules sometimes make two-dimensional arrangements, called films, monolayers, bilayers, etc. A film is a layer of substance spread so thin over a surface that gravitational effects are negligible. A monolayer or molecular film is a film considered to be only one molecule thick. If molecules, such as lecithin molecules, which each have a polar head and a long hydrocarbon tail, are involved in forming a film through a pinhole in a wall plate immersed in water, they may then orient themselves at the pinhole and form a film. The boundaries of which are covered with polar heads. Such arrangements causes their hydrocarbon tails to avoid directly meeting water. The film is, thus, composed of two monolayers with one turned-over to the other, so that their hydrocarbon sides are facing each other. This film is called a bilayer. Similar bilayers appear widely as biological cell membranes.

### 2.2.1 Gibbs' Monolayer

If the surface tension is lowered by addition of a solute, then, by the Gibbs equation, Eq. 2.17, the solute must be adsorbed at the interface, the amount being given by  $\Gamma_2^1$ , Eq. 2.27, under the Gibbs model. This adsorption may correspond to a monolayer. It is plausible to assume that the adsorbed solute molecules make a thermal motion, more or less, freely on the surface like gas molecules.

Figure 2.3 shows that  $\Gamma_2^1$  can be expanded as a power series of the activity,  $a_2$ . For low concentrations,  $\Gamma_2^1 \sim bc_2$ , where  $b$  is a constant. Eliminating  $c_2$  in Eq. 2.27, we can express the equation strictly in terms of surface quantities,  $\gamma$  and  $\Gamma_2^1$ . Integrating we have

$$\gamma_0 - \gamma = \Gamma_2^1 k_B T \quad (2.40)$$

where  $\gamma_0$  stands for the integration constant corresponding to the vanishing adsorption. Accordingly,  $\gamma_0$  is the surface tension of the pure solvent. Customarily, the quantity,  $\gamma_0 - \gamma$ , is called the surface pressure, denoted by  $\pi$ , which has the dimension of dyne/cm or erg/cm<sup>2</sup>. Noting that  $1/\Gamma_2^1$  represents the surface area per adsorbed molecule,  $A_m$ , Eq. 2.40 becomes

$$\pi A_m = k_B T \quad (2.41)$$

This is a two-dimensional version of the familiar equation of state for an ideal gas, in which molecules are point masses with no mutual interaction. However, the adsorbed molecules are of a finite size and interact each other. Following the van der Waals equation of state, Eq. 2.41 may be modified and we have

$$\left( \pi + \frac{a}{A_m^2} \right) (A_m - \omega_o) = k_B T \quad (2.42)$$

where  $a$  and  $\omega_o$  are constants. Here,  $\omega_o$  may be understood as the cross-sectional area of the molecule and the area,  $A_m$ , cannot be smaller than  $\omega_o$ . Because of this, there is a saturation,  $\Gamma_m$ , in the adsorption curve (Fig. 2.3). Intuitively,  $\omega_o \sim 1/\Gamma_m$ .

The surface tension has a dynamic behavior. When a new surface is created, it takes a finite time for the surface molecules to rearrange in a preferred orientation and distribution by diffusion before reaching equilibrium. The surface tension thus changes with time. If the change is slow, the dynamic surface tension can be easily measured by an ordinary method of, say, the Wilhelmy plate (Fig. 2.7). If the surface is rapidly compressed, there will temporarily be a more surface excess, increasing the surface pressure. The change will disappear by a partial diffusion of the molecules.

If the surface area changes (strain:  $dA/A$ ) without a change in the total surface excess moles, the surface pressure changes (stress:  $d\pi$ ). At constant temperature and pressure, the ratio of the stress to the strain defines a modulus,  $E$ , of surface dilatational elasticity. As long as the stress is small, we define

$$E = -A \frac{d\pi}{dA} = -\frac{d\pi}{d \ln A}, \quad (2.43)$$

where the negative sign appears to make  $E$  positive in view of Eq. 2.41. In Gibbs' monolayers,  $E=0$ , if the surface tension is in rapid equilibrium with a bulk solution. This is usually not so (Thomas and Potter, 1975), and in Eq. 2.43  $A$  may be replaced by  $A_m$  and, combining Eqs. 2.40, 2.41, and 2.43,  $E=k_B T \Gamma_2^1$  for an ideal and dilute solution. In general,  $E$  may be expanded in a power series

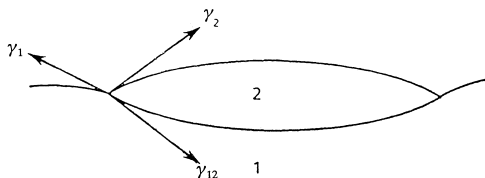
$$E = k_B \Gamma_2^1 - a_1 (\Gamma_2^1)^2 + a_2 (\Gamma_2^1)^3 \quad (2.44)$$

The elastic behavior usually becomes important when a surface deformation is time-dependent and is more pronounced in insoluble monolayers as discussed below.

In most cases, compression of a surface film introduces an increase in temperature, whereby the elasticity increases. (This is due to the entropy change at the compression.) Thus, the adiabatic elasticity is larger than the isothermal elasticity. The isothermal elasticity (Gibbs' elasticity) is determined by Eq. 2.44. The experimental determination is described by, for instance, Luccasen and Giles (1975).

### 2.2.2 Insoluble Monolayers

If a small oil drop is poured on the surface of water, it spreads easily and dampens surface waves or ripples in the water, if any. It has been understood that a small amount of oil can form a monolayer by spreading on the interface with water. It also changes the surface tension, the specific behavior of which can dampen the surface waves quickly.



**Fig. 2.6** Surface forces at point where three fluids meet.

The process of oil spreading on water is due to the surface tension. The oil is initially in the form of a deformed droplet on the water surface. As shown in Fig. 2.6, there are three different interfaces, 1, 2, and 12. At constant temperature and pressure, a small change in the surface free energy is given by

$$dG^s = \gamma_1 dA_1 + \gamma_2 dA_2 + \gamma_{12} dA_{12} \quad (2.45)$$

Note that there is no change in the total number of surface active molecules since they are insoluble. The area change must satisfy

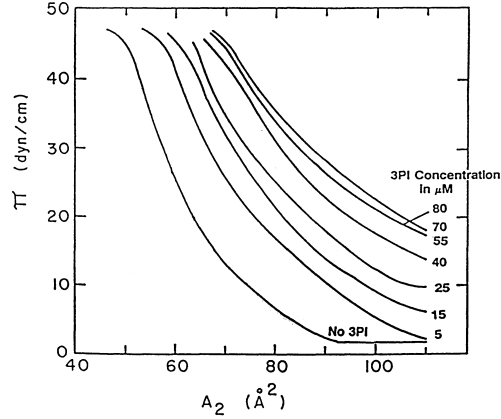
$$dA_1 = -dA_2 = -dA_{12} \quad (2.46)$$

Thus,

$$-dG^s/dA_2 = \gamma_1 - \gamma_2 - \gamma_{12} - S_{2/1} \quad (2.47)$$

The quantity,  $S_{2/1}$  or  $-dG^s/dA_2$ , must be positive in order for the droplet to spontaneously spread. This is called the spreading coefficient of 2 on 1. Note that  $dA_2$  is the change of the surface area 2. The spreading velocities depend on the substrate viscosity (Ahmad and Hansen, 1972) and is of the order of 15–30 cm/sec on water. It implies that films strongly interact with the bulk liquid phase.

Insoluble molecules have a deep potential well at the interface with the solvent so that they are trapped there to form a monolayer. A characteristic of insoluble monolayers is that their surface tension varies even when the film is very slowly expanded or compressed. The experimentally observed behavior of the surface tension is usually expressed in a  $\pi$ - $A_m$  isotherm, where  $\pi$  is the surface pressure defined by  $S_{2/1}$  with  $\gamma_{12}=0$ . Figure 2.7 shows an isotherm. We are dealing with monolayers only (a so-called liquid expanded region). If they are highly compressed, insoluble surface active molecules start most likely to build up.



**Fig. 2.7** Surface pressure versus surface area curves of an L- $\alpha$ -phosphatidylcholine/cholesterol monolayer with slightly soluble 3-phenylindole (3PI) concentrations. The curve for 80  $\mu\text{M}$  is nearly the same as that for 55  $\mu\text{M}$  within the experimental error in the range of the observation (Takeo, et al., 1984, with permission from Academic Press).

The surface tension of insoluble monolayers should obey Gibbs' formalism, even though they have at least a thickness of one molecule (usually long). By assuming that the surface is packed by surface molecules, we may write

$$A = \sum_i n_i^s \omega_i \quad (2.48)$$

where  $\omega_i$  is the partial molar surface area of component  $i$ , which is the cross-sectional area of the molecule. If the molecules are long, the cross-sectional area immersed in the solvent may depend on the temperature because of bending (Takeo et al., 1984). We denote the solvent by  $i=1$ . If all others are insoluble,  $n_i^s$  ( $i=2,3,\dots$ ) is fixed, remaining in the monolayer. Therefore, if the area  $A$  varies,  $n_1^s$  must change according to the relation:  $n_1^s = (A - n_2^s \omega_2 - n_3^s \omega_3 - \dots) / \omega_1$ . This change is responsible for the behavior of  $\gamma$ . From Eq. 2.23, at constant temperature and pressure we have

$$\omega_i d\gamma = -d\mu_i^s \quad (2.49)$$

We note that this expression does not explicitly show the surface concentration dependence. Since the molecules ( $i=2,3,\dots$ ) are insoluble, the chemical potential is almost discontinuous between the surface and bulk phases. In this sense, the chemical potential in Eq. 2.49 is explicitly expressed as that in the surface. (Of course, if the temperature is raised, the discontinuity may disappear.) In the present formalism, the change of the chemical potential leads to an intrinsic change in  $\gamma$ . In particular, we treat only the variation of component 1 for the present case. Since  $\mu_1^s = \mu_1^{0,s} + k_B T \ln a_1^s$ , after integration of Eq. 2.49 from the initial (pure solvent) to the final state, the surface pressure is given by

$$\pi = -\frac{k_B T}{\omega_1} \ln \frac{f_1^s x_1^s}{f_1 x_1} \quad (2.50)$$

where we have written the activity  $a_1$  in terms of the activity coefficient  $f_1$  and the molar fraction  $x_1$  for the initial pure state and the final state (with superscript s). For simplicity, suppose we have a three-component system. Then, we have

$$x_1^s = \frac{n_1^s}{\sum_{i=1}^3 n_i^s} = \frac{A - \sum_{i=2}^3 n_i^s \omega_i}{\omega_1 \sum_{i=1}^3 n_i^s} \quad (2.51)$$

Here, we are supposed to know  $\omega_i$  ( $i=1,2,3$ ), which may be found from the molecular structures or by experiments. For water,  $\omega_1=9.65$  Å at 25°C. In experiments, the numbers of insoluble molecules  $i=2$  and 3 are known, but the membrane area  $A$  is measured.

Since for the pure solvent, both  $f_1$  and  $x_1$  are unity, Eqs. 2.48 and 2.50 lead to

$$\pi = \frac{k_B T}{\omega_1} \ln \left( 1 + \frac{\omega_1}{A_m - \omega_o} \right) - \pi_o \quad (2.52)$$

where  $A_m$  is the average surface area of surface active molecules ( $A_m=A/(n_2^s+n_3^s)$ ). Other quantities are defined by

$$\omega_o = (n_2^s \omega_2 + n_3^s \omega_3)/(n_2^s + n_3^s) \quad (2.53)$$

$$\pi_o = -\ln f_1^s \quad (2.54)$$

For a large expanded surface, Eq. 2.52 can be written as

$$(\pi + \pi_o)(A_m - \omega_o) = k_B T \quad (2.55)$$

This is the same equation as Eq. 2.42. Equation 2.52 agrees fairly well with experimental  $\pi$ - $A_m$  isotherms in the liquid expanded state.

The surface elasticity has been defined by Eq. 2.44. The isothermal value can be found from the  $\pi$ - $A_m$  isotherm. However, we must note a relaxation phenomenon (Smith and Berg, 1980). The nonequilibrium elasticities measured by any dynamic method are known as Marangoni elasticities (Rusanov and Krotov, 1979; Malysa et al., 1981). They are associated with the surface dilatational viscosity (O'Brien and Lando, 1985; Runge and Yu, 1993).

Another dynamic behavior, called surface shear viscosity, also appears when the surface as a whole moves with speed  $v$  in the direction of  $y$ . The speed has a gradient  $dv_y/dx$  in the direction,  $x$ , perpendicular to  $y$ , both  $x$  and  $y$  directions being in the surface. There is then a drag on the faster moving element from the slower moving neighbor. If this gradient occurs over length,  $l$ , of the element along the direction of  $y$ , the drag is given by



$$f = \eta^s l \frac{dv_y}{dx}, \quad (2.56)$$

where  $\eta^s$  is the surface shear viscosity which is of the order of  $10^{-2}$  to  $10^{-4}$  g/sec or surface poises (sp) (Hansen, 1959). This surface shear viscosity is affected by the bulk viscosity of the solvent (Harkins and Kirkwood, 1938). In order to get some idea of the apparent bulk viscosity corresponding to  $\eta^s$ , consider that the monolayer (thickness  $\tau$ ) develops to a bulk fluid with viscosity,  $\eta$ . Then,  $\eta^s = \eta \cdot \tau$  and  $\eta$  has a value of the heavy grease. Rheologically, such viscous behavior is very important. The canal viscometer (Criddle, 1960) has been used for the measurement of  $\eta^s$ . This is a two-dimensional version of the Poiseuille method. Sano et al. (1986) has used a new optical method on the measurement at high frequencies.

The insoluble molecules (say, some surfactants) at the surface will have a concentration gradient when surface waves or ripples are present and the surface is subject to dilatation or contraction. A surface tension gradient results, causing the surface to flow to the region of higher surface tension. The viscous drag of this flow also carries liquid in the substrate (Marangoni effect). This additional effect causes a faster damping of surface waves in insoluble monolayers compared with Gibbs' monolayers (Lamb, 1945; Vines, 1960). Eisenmenger (1959) has suggested that the damping of waves at frequencies in the MHz range may be mainly due to effects of  $\eta^s$ , but the detailed mechanism is not yet known.

Some promising computer simulation of insoluble monolayers exists. The results are just getting to the stage of explaining some of the experimental findings (Karaborni, 1993).

For measurements of surface pressures, see Abraham et al. (1980). For physical structures including molecular orientations and chemical compositions, an infrared (reflection) and (resonant) Raman spectroscopic method has been used (Kuhn et al., 1972; Takenaka and Nakayama, 1976; Takenaka and Fukuzaki, 1979; Dluhy and Cornell, 1985; Raising et al., 1985; Sakai and Umemura, 1993). The detailed examination of the behavior of polarized light passing through or reflected by a monolayer allows the determination of the thickness of the inhomogeneous region, its refractive index, and its absorption coefficient (Ducharme et al., 1987). This approach is called as ellipsometry and widely used (Kawaguchi et al., 1988). Historically, an ultramicroscope was used to see heterogeneity such as patches of unspread material or of aggregates, with great sensitivity. Recently a fluorescence microscope has been used by adding a small amount ( $\sim 1$  mol percent) of fluorescent material to the monolayer (Miyano, 1989). Another development in the optical microscope is Brewster angle microscopy (BAM), which applies the principle that if p-polarized laser light is incident with a Brewster angle ( $\sim 53.1^\circ$ ) with respect to water surface it is not reflected and the monolayer can be observed (Hennon and Meunier, 1991; Hönig and Mäbius, 1991). The BAM has disclosed interesting structures (Siegel and Vollhardt, 1994; Weidmann et al., 1995).

Transmission electron microscopes can also be used after transfer to a suitable support (Ries and Swift, 1987). Electron, x-ray, and neutron diffraction studies have been used. Scanning tunnelling microscopes, atomic force microscopes, and friction force microscopes have been also used. Scanning surface potential micro-

scopes can be applied for measurements of the surface potential and of the distribution of the dielectric constant of a film placed on a conductive substrate. They are really powerful in a membrane research (Fujihira and Kawate, 1994). The scanning near-field optical microscope, which has a very high spatial resolution, will also produce interesting physical and chemical information on membranes (Pohl and Courjon, 1993).

There are various variations, in appearance, of insoluble monolayers. Insoluble monolayers have polarity with one side of the hydrophilic (water loving) polar heads and another side of the hydrophobic (water fearing) hydrocarbon tails. The monolayers are in contact with water on the hydrophilic side. If the concentration of single-chained surfactants, such as lysolecithin, in solution is larger than some value (the critical micelle concentration, Chapt. 9), they then aggregate spontaneously, in favor of entropy, into a form of a closed monolayer which appears as small closed spherical shells of about 40 Å in diameter (micelles). This is a process of self-assembly, which, as will be discussed in Chapt. 9, occurs when the chemical potential is smaller for the molecules in the aggregated state than in the monomer states. (Tanford, 1973 and 1980). The outer surface is the hydrophilic side facing the bulk water. The size is determined by the fact that the inner volume is just filled with hydrocarbon chains of the single-chained surfactants (see Sec. 9.4). If a drop of the surfactants of the type of a lecithin molecule, which has two hydrocarbon chains, covers a pinhole in a teflon plate, which is immersed in the bulk aqueous solution, the drop spreads and finally forms a membrane across the pinhole called a bilayer membrane. Both surfaces of the bilayer are occupied by the hydrophilic polar heads of the surfactants. The inner portion between the surfaces of the bilayer is filled with the hydrophobic hydrocarbon chains of the surfactants. The thickness is typically about 50 Å. Sonication of such bilayers can lead to a formation of spherical bilayer shells of about 1000 Å in diameter with bulk solution also inside the spherical bilayer (vesicle). There are also many varieties. For details, see Israelachvili et al. (1980), Szoka and Papahadjopoulos (1980), Israelachvili (1991), and Fuhrhop and König (1994).

Bilayers cannot be formed by lysolecithin molecules since the space inside cannot be filled by single-chained molecules. However, if a single chain has more complicated structures (like azobenzene groups) in the chain, then it can form a bilayer. It is sometimes energetically more favorable if bilayers appear in a form of vesicles by eliminating edges of otherwise planar bilayers. The favorable size is discussed by Israelachvili et al. (1976). Vesicles can be prepared in an aqueous solution. They have been found to have an ability of entrapping and transporting foreign materials. Thus, they can have important applications to be used for transporting drugs to specific biological systems (Gregoriadis et al., 1993).

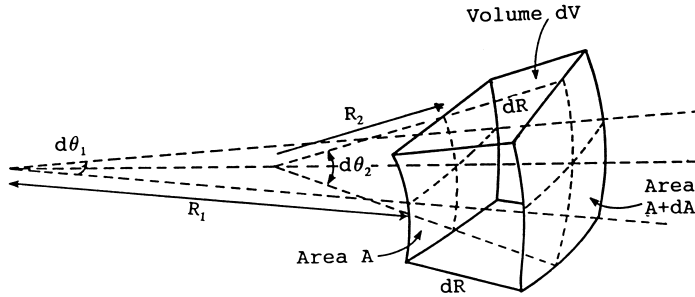
Membranes are most common cellular structures in animal cells and plant cells. These membranes are very complex, but artificial (phospholipid, glycolipid, etc.) bilayers have been used as their models for a selective transport mechanism of ions and neutral molecules in biophysical research (Marsh, 1990). Their physical and thermodynamic properties are discussed by Evans and Needham (1987). In particular, there is a recent development on an ionic channel transport in membranes (Westmark and Smith, 1994).

## Exercises

- 2.1 Show that  $dF=0$  for a thermodynamic isothermal process at constant volume.  
 2.2 Associated with Eq. 2.11, we considered a bubble in a liquid. What happens with this equation if a liquid drop is in the atmosphere of its vapor, instead?  
 2.3 Consider, as an example of Eq. 2.11, a curved surface where the local principal radii of curvature are  $R_1$  and  $R_2$  and the relation (Young-Laplace equation):

$$p'' - p' = \gamma \cdot \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$

holds locally. Show that Eq. 2.11 is satisfied for this surface. (Note that  $dA = [(1/R_1) + (1/R_2)]dV''$ . See the figure below.)



$$(dV = (R_1 d\theta_1) \cdot (R_2 d\theta_2) \cdot dR = R_1 R_2 dR d\theta_1 d\theta_2, dA = (A + dA) - A \sim (R_1 + R_2) dR d\theta_1 d\theta_2)$$

- 2.4 A spherical droplet of liquid, denoted by (''), of radius,  $a$ , is in the vapor denoted by ('). We refer to the molar entropies and volumes ( $S'_m = S'/n'$ ,  $V'_m = V'/n'$ , with  $n'$  moles in  $V'$ , etc.). Write the Gibbs-Duhem equations separately for the two phases. Then, show that in equilibrium at constant temperature

$$V'_m dp' = V''_m dp''$$

Next, show that, since  $V'_m = RT/p'$  and  $p'' - p' = 2\gamma/a$ , where  $R$  is the gas constant, the equilibrium vapor pressure satisfies

$$\ln(p'/p_\infty) = 2\gamma V''_m / aRT, \text{ if } V'_m \gg V''_m$$

Here,  $p_\infty$  is the vapor pressure at the surface of a drop of  $a \rightarrow \infty$  (a flat surface where equilibrium vapor pressure is  $p_\infty$ ).

- 2.5 Consider a bubble of radius  $10^{-5}$  cm in water, when the water phase is at the pressure of one atmosphere. Is the bubble stable? Assume that the vapor pressure is at 0.1 MPa and the surface tension is 59 dyne/cm (100°C).  
 2.6 Consider a two-phase one component system in equilibrium. The two phases may be a liquid drop of volume,  $V'$ , at pressure,  $p'$ , and the vapor of volume,  $V''$ , at  $p''$ , which is surrounding the drop. If the volume,  $V_t$  of the total system is changed by a work,  $-p''dV_t$ , on the system from outside, both  $V'$  and  $V''$  must accordingly change

( $dV=dV'+dV''$ ). The external work must also cause the change of the interfacial area by  $dA$  between the drop and the vapor. Then, show that

$$-p''dV = -p'dV' - p''dV'' + \gamma dA$$

(This relation holds for any two-phase system.)

- 2.7** We have derived Eq. 2.15 by keeping  $T$ ,  $p'$ ,  $p''$ , etc. unchanged. However, the equation generally holds. Why? ( $U$  is a homogeneous function of  $S$ ,  $V'$ ,... for any change of independent variables.)
- 2.8** Derive Eq. 2.19 from Eqs. 2.14 and 2.16 for a one-component system.
- 2.9** Show that the surface tension is the surface Gibbs free energy per unit area (Eq. 2.20).
- 2.10** In Eq. 2.26,  $d\gamma$  seems to be independent of  $d\mu_1$  due to an arbitrary choice of  $\Gamma_1$  as null. Does  $d\mu_1$  depend on  $d\mu_2$ ? (Note that  $\Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 = \Gamma_2^1 d\mu_2$ .)
- 2.11** In Eq. 2.27,  $c_2$  must be replaced by the activity,  $a_2$ . If  $a_2$  is rewritten by introducing the activity coefficient,  $f_2$ , such that  $a_2 = f_2 x_2$  with the molar fraction,  $x_2$ , of the component 2, show that

$$\Gamma_2^1 = -\frac{x_2}{k_B T} \frac{d\gamma}{dx_2} \left( 1 + \frac{d \ln f_2}{d \ln x_2} \right)^{-1}$$

Here,  $d \ln f_2 / d \ln x_2$  is a correction factor. (Note that from Eq. 2.26  $d\gamma = -\Gamma_2^1 (d \ln f_2 + d \ln x_2)$ .)

- 2.12** If two phases, ' and ', of solvents 1 and 2 are in contact at constant  $T$ ,  $p'$ , and  $p''$ ,  $\sum n_i' d\mu_i = 0$  and  $\sum n_i'' d\mu_i = 0$  from Eq. 2.16. We may use the convention, Eq. 2.29 ( $\Gamma_1 = \Gamma_2 = 0$ ) and assume that the solvents can mix. If solute 3 is distributed among them, show that the surface excess of solute 3 relative to solvents 1 and 2 is given by

$$\Gamma_3^{1,2} = \Gamma_3 - \frac{\Gamma_1 (n_2'' n_3' - n_2' n_3'') - \Gamma_2 (n_1'' n_3' - n_1' n_3'')}{n_2'' n_1' - n_2' n_1''}$$

(Hint: in this derivation, refer to Eq. 2.25 and use the Gibbs-Duhem equations to eliminate  $d\mu_1$  and  $d\mu_2$ .) The relation can handle a realistic case as indicated bellow. Solvents 1 and 2 are water and oil, respectively, and partially in the oil phase, ', and partially in water phase, '. The amount present in each phase is given in moles, referring to the area of  $260 \text{ cm}^2$ .

Oil phase	$n_1'' = 0.09$ ,	$n_2'' = 0.96$ ,	$n_3'' = 0.24$
Surface	$n_1^s = 1.02$ ,	$n_2^s = 0.86$ ,	$n_3^s = 0.51$
Water phase	$n_1' = 1.08$ ,	$n_2' = 0.36$ ,	$n_3' = 0.18$

Find the surface excess of solute 3 for this case, relative to both oil and water.

- 2.13** Suppose that the density profile is given as a function of height as  $p(z)$  in the normal direction to the liquid-vapor interface. If the location  $z = z_0$  of the Gibbs dividing surface satisfies

$$\int_{z_l}^{z_0} [\rho_l - \rho(z)] dz = \int_{z_0}^{z_v} [\rho(z) - \rho_v] dz$$

how does the plane  $z=z_0$  divide the surface density? Verify your statement by using Eq. 2.36.

**2.14** Establish Eq. 2.40.

**2.15** An adsorption equation known as the Frumkin isotherm (1925) has the form:

$$\ln \Gamma_2^1 - \ln(\Gamma_m - \Gamma_2^1) + a\Gamma_2^1/\Gamma_m = \ln(bc_2), \quad (a, b: \text{constants})$$

when  $\Gamma_2^1 \ll \Gamma_m$ ,  $\Gamma_m$  being the limiting value of  $\Gamma_2^1$ . Show what the corresponding two-dimensional equation of state is. That is, show what corresponding relationship is between  $\pi$  and  $1/\Gamma_2^1$ . (Hint: differentiate the equation to eliminate  $b$ . Then, use Eq. 2.27 to eliminate  $c_2$  and integrate. Note that  $\pi = \gamma_o - \gamma$ .)

**2.16** Rewrite Eq. 2.42 for one mole of adsorbed molecules.

**2.17** If the surface (total area:  $A$ ) of a solution containing a surface active solute is expanded suddenly by  $dA$ , what is the change in the area per adsorbed solute molecule before any more adsorption from the solution occurs? (This is the case with an insoluble monolayer.) Then, what is the surface pressure? Assume the van der Waals equation of state (Eq. 2.55).

**2.18** In Eq. 2.50, what kind of choice is made for the Gibbs dividing surface (Lucassen-Reynders, 1976)? (If insoluble surfactants are involved, the problem is greatly simplified. The total amount of surfactants in the surface phase do not change even though the surface area changes. Thus,  $d\gamma = -(1/\omega_1)d\mu_1$  (1 for the solvent, Eq. 2.49). This is equivalent to the choice of  $\Gamma_i = 0$  with  $i=2,3,\dots$ ).

**2.19** In a spherical micelle, the radius cannot be larger than the so-called critical (maximum effective) length,  $l_c$ , of the hydrocarbon chain. If the chain has  $n$   $\text{CH}_2$  groups,  $l_c$  is approximately given by  $0.154 + 0.1265n$  nm (Tanford, 1973 and 1980). The volume,  $v$ , per chain is also given as  $(27.4 + 26.9n) \times 10^{-3}$  nm<sup>3</sup>. Then,  $a_o = v/l_c$  is the surface area on the micelle surface per molecule. First show, assuming the packing of the micelle with the chains, that  $(v/a_o l_c) < 1/3$  for micelle formation. Then, find the mean aggregation number (the number of molecules per micelle) when  $n=12$  (see Sec. 9.4).

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